



Title: Quality Assurance and Quality Control Requirements and Performance Standards for the Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)

WSC – CAM – IV A

Quality Assurance and Quality Control Requirements for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP-VPH-04-1.1 for the Massachusetts Contingency Plan (MCP)

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IV. Petroleum Hydrocarbon Methods

A. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP-VPH-04-1.1, May 2004

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1.0 QA/QC Requirements for the Volatile Petroleum Hydrocarbon Method

1.1 Method Overview

The Volatile Petroleum Hydrocarbons Method, MADEP-VPH-04-1.1, (the "VPH Method") uses purge-and-trap sample concentration, gas chromatographic (GC) separation and in-series Photoionization and Flame Ionization Detectors (PID/FID) to identify and quantify both target analytes and method-defined aliphatic and aromatic hydrocarbon fractional ranges in water, soils and sediments. Volatile aliphatic hydrocarbons are collectively quantified within two specific ranges: C₅ through C₈, and C₉ through C₁₂. Volatile aromatic hydrocarbons are collectively quantified within the C₉ to C₁₀ range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C. This method may also be used to identify and quantify benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) as Target Analytes. All references to SW-846 Methods in this document refer to the United States Environmental Protection Agency's most recently published version.

The VPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons entitled "Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter (MADEP Interim Final, August, 1994) and the "Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology" (MADEP January, 2003). It is intended to produce data in a format suitable for evaluation by that approach, and that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

Petroleum products suitable for evaluation by the VPH Method include gasoline, mineral spirits, and certain petroleum naphthas. In and of itself, the VPH Method is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products, which contain higher boiling components, or distillates of aliphatic and/or aromatic hydrocarbons that are beyond the analytical range of the VPH Method.

1.1.1 Reporting Limits for the VPH Method

The Reporting Limit (RL) for each of the aliphatic and aromatic fractional ranges is approximately 5 - 10 mg/kg in soil/sediment, and approximately 100 - 150 µg/L in water for the VPH Method. The RL of this method for Target Analytes is compound-specific, and ranges from approximately 0.05 - 0.25 mg/kg in soil/sediment, and 1 - 5 µg/L in water. These RLs reflect the sampling procedures and the prescriptive analytical conditions imposed by the Method. The RLs are dependent on the concentration of the lowest analytical standard in the initial calibration and/or percent solids of the sample.

Preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for VPH samples analyzed in support of MCP



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decision-making are presented in Appendix IV A-1 of this document and Appendix VII-A of WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 Summary of VPH Method Quality Control Requirements

Each laboratory that uses the VPH Method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control samples (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of the laboratory or at the request of the data-user.

Laboratories must document and have on file an Initial Demonstration of Laboratory Capability for each combination of sample preparation and determinative method being used. An IDLC must be completed and documented when a method is initially started up, whenever a method is substantially modified or new laboratory staff is trained to perform the VPH Method. Procedural requirements for performing the Initial Demonstration of Laboratory Capability can be found in SW-846 Method 8000B (Section 8.4) and Appendix 7 of the VPH Method. The data associated with the Initial Demonstration of Laboratory Capability should be kept on file at the laboratory and made available to potential data users on request.

Note: Because of the inherent difficulty in quantifying fractional hydrocarbon ranges and the number of QC elements associated with the Initial Demonstration of Laboratory Capability, it should be expected that one or more of the ranges and/or target analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all nonconformances. All nonconformances, along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Capability data. This information should be kept on-file at the laboratory.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table IV A-2 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the VPH Method, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table IV A-2. It should be noted that the performance standards listed in Table IV A-2 are based on multiple-laboratory data, which are in most cases expected to demonstrate



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more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. A list of the required VPH Method performance standard elements and method references is presented below.

Performance Standard Element	Method Reference
Initial Calibration	The VPH Method, Section 11.1
Continuing Calibration	The VPH Method, Section 10.4.2.1
Laboratory Method Blanks	The VPH Method, Section 10.4.2.2
Laboratory Control Sample (LCS)	The VPH Method, Section 10.4.2.3
LCS Duplicates	The VPH Method, Section 10.4.2.4
Surrogate Recovery	The VPH Method, Section 7.5

In some cases, the standard laboratory acceptance criteria for the various QC elements may have to be modified to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs (GCs), and skilled in the interpretation of gas chromatograms for individual target analytes and petroleum hydrocarbon ranges in environmental matrices. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results both for individual target analytes and petroleum hydrocarbon ranges with this method.

1.1.3 Sample Introduction Methods

As prescribed in Section 9.1 of the VPH Method, samples for analysis are introduced into the gas chromatographic system using a purge-and-trap concentrator as described in SW-846 Methods 5030B and 5035A for aqueous and solid samples, respectively. If other sample introduction methods are utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the analytical case narrative.

1.2 Summary of Method

The VPH Method is suitable for the analysis of waters, soils, sediments and NAPL. The method includes inert gas purging, of an aqueous sample or soil methanol extract, with concentration onto an adsorbent trap, and subsequent analyses by gas chromatography.

The VPH Method is based on (1) SW-846 Methods 5030B, 5035A, 8000B, 8021B, and 8015B, (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November 1990; and (3) "Modified GRO Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.



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The gas chromatograph oven is temperature-programmed to facilitate separation of the analytes of interest. Detection is achieved by using a photoionization detector (PID) and flame ionization detector (FID) operating in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of volatile aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of Target Analytes (BTEX/MTBE/naphthalene) and collective concentration of aromatic hydrocarbons within the C₉ through C₁₀ range. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C₅ through C₈ and C₉ through C₁₂ ranges. The VPH method marker compounds and retention time windows are summarized in Table IV A-1.

Table IV A-1 VPH Method Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C ₅ -C ₈ Aliphatic Hydrocarbons (FID)	0.1 minutes before n-Pentane	0.1 minutes before n-Nonane
C ₉ -C ₁₂ Aliphatic Hydrocarbons (FID)	0.1 minutes before n- Nonane	0.1 minutes before Naphthalene
C ₉ -C ₁₀ Aromatic Hydrocarbons (PID)	0.1 minute after o-Xylene	0.1 minutes before Naphthalene

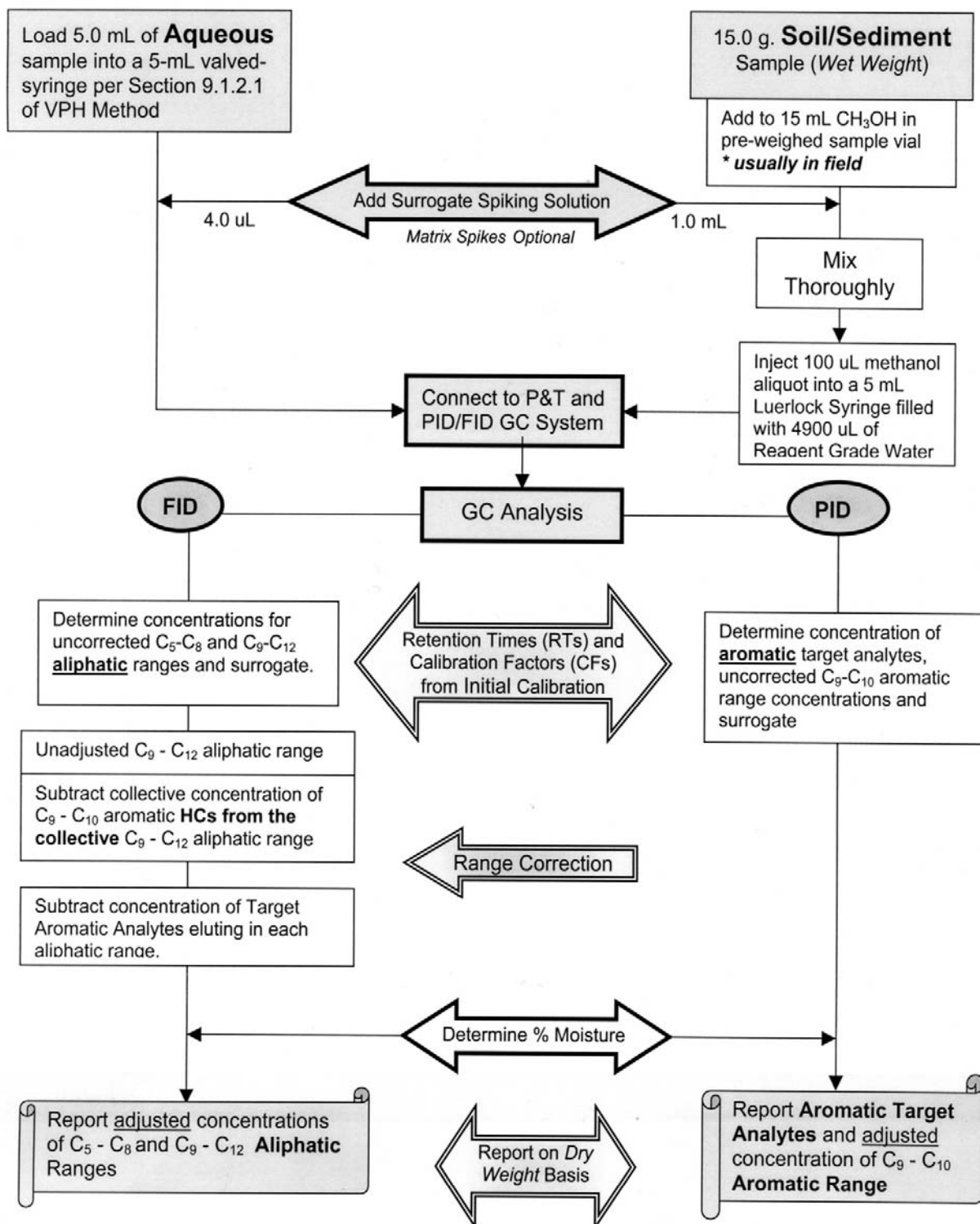
1.2.1 VPH Sample Analysis

A flow diagram for the VPH analytical process for aqueous and soil/sediment samples using a five-point external calibration and 2,5-Dibromotoluene as a surrogate is presented in Figure IV A-1.



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Figure IV A-1 Volatile Petroleum Hydrocarbon (VPH) Analytical Process





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1.2.1.1 Analysis of Water Samples

Water samples may be analyzed directly without sample preparation. The analysis of water samples is described in detail in Section 9.1.2 of the VPH Method. In general, a sample aliquot is introduced to the purge chamber using a 5 mL gas-tight syringe. If necessary, samples may be diluted prior to injection into the purge chamber. In such cases, sample dilutions must be performed as expeditiously as possible and the diluted sample should be transferred to a gas-tight syringe without delay.

1.2.1.2 Analysis of Soil and Sediment Samples

Soil and sediment samples are dispersed in methanol to extract the volatile organic constituents. A portion of the methanol extract is then extracted/concentrated by purge-and-trap and analyzed by GC. Methanol may be added in the field or in the laboratory if the samples are collected in specially designed air-tight samplers. The desired ratio of methanol-to-soil is 1 mL methanol/1 gram soil, +/- 25%. Highly-organic matrices (e.g., peat) may require additional methanol (up to 2 mL per gram of soil). In either case, an aliquot of the methanol extract is added to reagent water to produce a 5 mL adjusted sample volume and introduced into the gas chromatograph using a purge and trap concentrator. The volume of the aliquot will depend on the anticipated VPH concentration. ***Be advised that the volume of methanol aliquot added should not exceed 200 μ L to preclude adverse solvent front and trap breakthrough difficulties.***

1.3 VPH Method Interferences

1.3.1 Chemical Contaminants

Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of system contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences and/or false positives.

Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should determine the cause of the contamination before re-analysis occurs. Corrective actions may include changing the purge gas source and/or regenerating the molecular sieve purge gas filter. **Subtracting blank values from sample results is not permitted.** If the laboratory determines that the concentration reported in the blank is so high that false positive results are likely in the associated samples, then the laboratory should fully explain this situation in the Environmental Laboratory case narrative.

1.3.2 Cross- Contamination/Carryover



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Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds (including VPH target analytes and ranges), one or more blanks should be analyzed to check for potential cross-contamination/carryover. The laboratory must determine individual VOC concentrations that cause a cross-contamination/carryover condition. Manifestation of this condition is dependent upon the concentration and level of detector saturation for the particular analyte. Concentrations of VOCs, which exceed the upper limit of calibration, should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later sample run.

1.3.3 Other Potential Interferences

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and chlorofluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water (for aqueous samples) or methanol (for soil and sediment samples), and carried through sampling and handling protocols, serves as a check on such contamination.

1.3.4 General Precautions

As a general precaution, the laboratory where VPH and other volatile analyses are performed should be completely free of uncontained solvents. The analytical and sample storage areas should be isolated from all sources of potentially interfering volatile organics. All GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to potentially interfering volatile organics during common laboratory activities can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random elevated background concentrations of volatile organics and the same precautions must be taken.

1.4 Quality Control Requirements for the VPH Method

1.4.1 General Quality Control Requirements for Determinative Chromatographic Methods

Refer to SW-846 Method 8000 for general quality control procedures for all chromatographic methods, including the VPH Method. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data.

Quality Control procedures necessary to evaluate the GC system operation may be found in the VPH Method, Section 10.2 and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance



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requirements for the analytical system may be found in the VPH Method, Sections 10.0 and 13.0, respectively.

1.4.2 Specific QA/QC Requirements and Performance Standards for the VPH Method

Specific QA/QC requirements and performance standards for the VPH Method are presented in Table IV A-2. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with “Presumptive Certainty” regarding the usability of analytical data to support MCP decisions. The concept of “Presumptive Certainty” is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of “Presumptive Certainty” of data acceptance by agency reviewers. In order to achieve “Presumptive Certainty” for the VPH Method, parties must:

- (a) Comply with the procedures described and referenced in WSC-CAM–IV A;
- (b) Comply with the applicable QC analytical requirements prescribed in Table IV A-2 for this test procedure;
- (c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table IV A-2 for this test method; and
- (d) Adopt the reporting formats and elements specified in the CAM and in Appendix 3 of the VPH Method

In achieving “Presumptive Certainty” status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment

Widespread adherence to the “Presumptive Certainty” approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the “Presumptive Certainty” option have an obligation, pursuant to 310



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CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

1.4.3 Use of Surrogates, and Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) with Methanol-Preserved Soil/Sediment Samples

The recovery of surrogates and matrix spikes from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. Quality Control parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation and quantitation).

Because of this limitation, it is recommended that the laboratory consider adopting alternative quality control elements for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies. Recommended practices for additional quality assurance may be found in SW-846 Methods 5000 and 8000B.

This inherent limitation associated with the evaluation of matrix spike and surrogate recoveries attributable to methanol preservation of soil and sediment samples is more than compensated for by the marked improvement in sample integrity and conservation/recoveries of the volatile analytes of concern from soil and sediment matrices.

1.4.4 Special Analytical Considerations - Addition of Surrogates and Full Matrix Spikes

Appropriate surrogates and full matrix spikes must be added to the methanol extract through the septum seal prior to equilibration of the sample to room temperature. All samples should be shaken for 2 minutes to assure adequate mixing prior to analysis. A 100 microliter (µL) aliquot (or other appropriate volume) of the methanol extract must then be removed and added to reagent water to provide a 5 mL "adjusted" sample volume.

1.4.5 Trip Blanks and Field Duplicates for VPH Analyses

As described in WSC-CAM VII A, Section 2.5, Table VII A-1, a Trip Blank for each cooler and submission of Field Duplicates are recommended for drinking water samples only. However, the Field Duplicates need only be analyzed if the concentration of one or more VPH target analytes or ranges in the primary sample is above the Reporting Limit (RL). The Trip Blank need only be analyzed if the concentration of one or more VPH target analytes or ranges in any sample transported in the same cooler is above the Reporting Limit. Drinking water samples should be identified and specific analytical instruction for the drinking water and associated field quality control samples provided when the samples are submitted to the laboratory for analysis



Table IV A-2 Specific QA/QC Requirements and Performance Standards for the VPH Method

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
GC Performance	Inter-laboratory consistency and comparability	(1) n-Pentane and MTBE must be resolved from solvent front. (2) Surrogate standards must be resolved from target compounds.	No	Perform instrument/injection port maintenance as necessary.	Suspend all analyses until performance criteria are achieved. Report exceedances in the Environmental Laboratory case narrative.
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed (2) Calculated according to the method. (Section 9.3) (3) Retention time windows must be updated with every CCAL.	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards (2) Low standard must be \leq reporting limit (RL) (3) %RSD should be ≤ 25 or "r" should be ≥ 0.99 for all compounds and ranges. (4) Must contain all VPH range and target analytes (5) If regression analysis is used, the curve must not be forced through the origin. (6) Must meet GC performance standards.	No	Recalibrate as required by method.	Sample analysis may not proceed without a valid initial calibration. Report exceedances in Environmental Laboratory case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Every 24 hours, prior to samples, and after no more than 20 samples. (2) Concentration level near midpoint of curve (3) Must contain all VPH range and target analytes (4) Percent Difference or Percent Drift must be ≤ 25 for all target compounds and ranges except for nonane, which should be ≤ 30 . (5) CCAL must meet GC performance standards.	No	Recalibrate as required by method. Any samples analyzed between the last CCAL that meets criteria and the one that fails criteria must be reanalyzed.	Report exceedances in Environmental Laboratory case narrative.
Laboratory Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil) (3) VPH ranges must be $< 10\%$ of the most stringent applicable MCP standard and Target analytes must be $< RL$ (4) Hydrocarbon ranges must be $\leq 10\%$ of the most stringent applicable MCP cleanup standard.	Yes	Locate source of contamination; correct problem; re-analyze method blank. Any samples analyzed between the last valid method blank and the method blank that fails criteria must be re-analyzed.	(1) Report non-conformances in Environmental Laboratory case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention, should qualify the sample results. Blank contamination should also be documented in the Environmental Laboratory case narrative (3) If re-analysis is performed within holding time, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time, the laboratory must report results of both the initial analysis and the reanalysis.



Table IV A-2 Specific QA/QC Requirements and Performance Standards for the VPH Method (*continued*)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Must contain all VPH target analytes and ranges. (4) Concentration level should be between low and mid-level standard. (5) Matrix-specific (e.g., soil, water) (6) Laboratory-determined percent recoveries must be between 70 – 130 for VPH ranges and target compounds except for nonane, which should be between 30-130. (7) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Re-calculate the percent recoveries; Re-analyze the LCS; Locate source of non-conformance; Re-analyze associated samples.	(1) Report nonconformances in Environmental Laboratory case narrative. (2) If re-analysis is performed within holding time, the laboratory may report results of the reanalysis only. (3) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and the reanalysis.
LCS Duplicate	Laboratory Method Precision	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all VPH target analytes and ranges. (4) Recommended to be run immediately after LCS in analytical sequence. (5) Laboratory-determined percent recoveries must be between 70 – 130 for VPH ranges and target compounds except for nonane, which should be between 30-130. (6) Matrix-specific (e.g., water, soil). (7) Laboratory-determined Relative Percent Difference (RPD) must be ≤ 25 for VPH ranges and target analytes	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data-user) (2) Matrix-specific (3) Prepared by fortifying field sample with standard from source different than source used for initial calibration (4) Concentration level - between low (RL) and mid-level (50%) standard (5) Must contain all VPH ranges and target analytes. (6) Percent recoveries - between 70 – 130 except for nonane, which should be between 30-130. (7) RPDs should be ≤ 50 for waters and solids	Yes Only when requested by the data-user	Check LCS; if recoveries acceptable in LCS, narrate non-conformance.	Note exceedances in Environmental Laboratory case narrative.
Matrix Duplicate	Method Precision in Sample Matrix	(1) Analyzed with every 20 samples (optional) (2) Matrix-specific (3) RPD should be ≤ 50 for results $> 5 \times \text{RL}$.	Yes Only when requested by the data-user	Recheck sample calculations. Re-analyze associated samples.	Note exceedances in Environmental Laboratory case narrative.

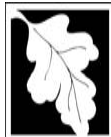


Table IV A-2 Specific QA/QC Requirements and Performance Standards for the VPH Method (*continued*)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	(1) Minimum of 1 method surrogate. Recommended surrogate: 2,5-dibromotoluene. (2) Percent recoveries must be between 70-130 on both detectors. (3) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above.	Yes	If one or more surrogates are outside limits, reanalyze sample unless one of the following exceptions applies: (1) obvious interference present (e.g., UCM). (2) for methanol-preserved samples, reanalysis is not required if % moisture >25 and recovery is >10%. (3) if one surrogate exhibits high recovery and target analytes are not detected in sample.	(1) Note exceedances in case narrative. (2) If reanalysis yields similar surrogate nonconformances, the laboratory should report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial and reanalysis. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
General Reporting Issues	NA	(1) The laboratory must only report values \geq the sample-specific reporting limit. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the <u>lowest</u> dilution within the valid calibration range for <u>each</u> analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) All information required in Appendix 3 of the method must be provided for each sample in a "clear and concise manner."			(1) Complete analytical documentation for diluted and undiluted analyses is to be available for review during audit; (2) All soil/sediment sample results must be corrected for methanol dilution. See Section 9.6.2.2 of the VPH Method (3) All soil/sediment sample results must be reported on a dry weight basis. See Section 9.6.2.1 of the VPH Method (4) All dilutions must be documented in the Environmental Laboratory case narrative.
<div>GC = Gas Chromatography MS = Matrix Spike %RSD = Percent Relative Standard Deviation NA = Not Applicable</div> <div>"r" = Correlation Coefficient RPDs = Relative Percent Differences UCM = Unresolved Complex Mixture</div>					



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1.5 Analyte List for the VPH Method

As described in Section 1.1, the VPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons entitled "Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter (MAPEP Interim Final, August, 1994) and the "Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology" (MADEP January, 2003). It is intended to produce data in a format suitable for evaluation by that approach, and that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

The MCP analyte list for the VPH Method is presented in Table IV A-3. The list is comprised of three (3) collectively quantified volatile hydrocarbon ranges and eight (8) Target Analytes, as identified in Section 3.0 of the VPH Method, that are readily-analyzable by the method using conventional purge-and-trap sample introduction via SW-846 Methods 5030B (ambient temperature) and/or 5035A for aqueous and solid samples, respectively. All the Target Analytes and hydrocarbon ranges that comprise the MCP Analyte List for the VPH Method have hydrocarbon range (e.g., C₉ – C₁₀ aromatic hydrocarbons) or compound-specific MCP Method 1 Groundwater/Soil Standards as described in 310 CMR 40.0974 and 40.0980, respectively. Use of the VPH Method to identify and quantify the listed Target Analytes is optional at the discretion of the LSP.

The MCP Method 1 Groundwater/Soil Standards used to characterize the risk of harm posed by oil or hazardous materials at a disposal site are described in 310 CMR 40.0974(2), Table 1. This list of groundwater/soil standards, developed by the Department, takes into account a defined set of conservative potential exposure pathways likely to be encountered at most disposal sites. Method 1 Standards have been developed by the Department for over one hundred organic and inorganic contaminants that are commonly encountered at disposal sites.

1.5.1 Additional Reporting Requirements for the VPH Method

While it is not necessary to request and report all the VPH Target Analytes listed in Table IV A-3, it is required to quantify the VPH aliphatic and aromatic hydrocarbon ranges, in the same table, to obtain Presumptive Certainty status. Such limitations must be documented for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials as described in Section 2.3.2 of WSC-CAM-VII A, Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP).

The Reporting Limit (based on the concentration of the lowest calibration standard) for each VPH hydrocarbon range or Target Analyte must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, background, etc.). Meeting "MCP program" reporting limits may require analytical modifications, such as increased sampling weight or volume, to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.



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Table IV A-3 Analyte List for the VPH Method

Range/Target Analyte	CASN	MCP CLEANUP STANDARDS	
		GW-1 (GW-2)	S-1/GW-1
		µg/L (ppb)	µg/g (ppm)
<i>Volatile Petroleum Hydrocarbon Ranges:</i>			
C ₅ -C ₈ Aliphatic Hydrocarbons	NA ¹	400	100
C ₉ -C ₁₂ Aliphatic Hydrocarbons	NA ¹	(1000)	1000
C ₉ -C ₁₀ Aromatic Hydrocarbons	NA ¹	200	100
<i>Target Analytes:</i>			
Benzene	71432	5	10
Ethylbenzene	100414	700	80
Methyl-tert-butylether (MTBE)	1634044	70	0.3
Naphthalene	91203	20	4
Toluene	108883	1000	90
o-Xylene ³	95476	(6,000)	500
m- Xylene ^{2,3}	108383	(6,000)	500
p- Xylene ^{2,3}	106423	(6,000)	500
<i>1.NA = Not Applicable</i>			
<i>2. May not be resolvable under chromatographic conditions required under this Method</i>			
<i>3. May be reported and evaluated as mixed isomers</i>			

2.0 Data Usability Assessment for the VPH Method

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for the VPH Method, which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

2.1 Specific Guidance Regarding the Interpretation and Use of VPH Data

The VPH Method produces both analyte-specific (target analytes) and method defined (hydrocarbon fractions) data. An analyte-specific approach produces data by comparing the response of a known analyte with an unknown concentration to the response of a standard for the same analyte with a known concentration under the same analytical conditions. A method-defined approach produces data by prescriptively defining both analytical conditions and



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assumptions used to calibrate and interpret the data produced. Such an approach is particularly useful in determining average characteristics for a limited set of analytes with similar physical, chemical and toxicological properties (i.e., the collective concentration of a limited range of hydrocarbons). However, a clear understanding of the analytical limitations of the method and assumptions used to interpret data are required to maximize the potential of using this approach.

Both VPH Target Analytes and hydrocarbon ranges are subject to potential "false positive" bias associated with non-specific gas chromatographic analysis. That is (1) other compounds co-eluting at the specified retention time may be incorrectly identified and/or quantified (false positive) as a Target Analyte; (2) compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions defined in Sections 3.4, 3.5 and 3.6 of the VPH Method, that may elute within the method-defined retention time window would be included in the Peak Area Calculation (PAC) and result in an overestimation of a fraction's concentration; or, (3) as described in Section 4.3 of the VPH Method, non-aromatic compounds that may elute between o-xylene and naphthalene and elicit a positive response on the PID would be included in the PAC, resulting in an overestimation of the C₉ through C₁₀ aromatic fraction's concentration.

Confirmatory analysis by a Gas Chromatography/Mass Spectroscopy (GC/MS) procedure or other suitable method, is recommended in cases where a VPH Target Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a hydrocarbon compound not meeting the regulatory definition of a specific hydrocarbon fraction is suspected. Dual-column confirmation is suitable for Target Analytes only.

The following definitions are provided to assist in the interpretation and evaluation of Volatile Petroleum Hydrocarbon data:

Aliphatic Hydrocarbon: Any organic compound comprised solely of carbon and hydrogen characterized by a straight, branched or cyclic chain of carbon atoms. By definition, this class of organic compounds includes alkanes, alkenes, alkynes, cycloalkanes or cycloalkenes for the VPH methodology.

Aromatic Hydrocarbon: Any cyclic and conjugated organic compound comprised solely of carbon and hydrogen. Aromatic compounds of environmental significance are benzoids that contain benzene or fused benzene rings.

Volatile Petroleum Hydrocarbon: Any hydrocarbon that elutes within the C₅ through C₈, and C₉ through C₁₂ aliphatic ranges or the C₉ through C₁₀ aromatic ranges defined by the method. The definition of Volatile Petroleum Hydrocarbon specifically **excludes** all substituted aliphatic or aromatic hydrocarbon derivatives (non-hydrocarbons as defined by the VPH Method), the individual VPH Method Target Analytes and/or surrogates that co-elute within these method-specific ranges. The VPH Method is suitable for the separation and quantification of the aliphatic and non-target aromatic components of gasoline, mineral spirits, certain petroleum naphthas and components of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products contained within the aforementioned method-defined ranges.

2.1.1 Interfering Peaks in Specified Aliphatic Hydrocarbon Ranges



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Hydrocarbons (and non-hydrocarbons), even with elution times within the defined chromatographic windows for the aliphatic hydrocarbon ranges specified by the VPH Method, need not be included in the PAC for these ranges unless they meet the definitions of aliphatic hydrocarbon and volatile petroleum hydrocarbon, as defined above. If the concentration of a hydrocarbon range is based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern is not apparent, the laboratory should provide this information and alert the data user of the potential for a false positive result in the Environmental Laboratory case narrative. MCP sites with chlorinated hydrocarbons, ketones, and/or co-mingled non-petroleum hydrocarbons are subject to this interference.

2.1.2 Interfering Peaks in Specified Aromatic Hydrocarbon Range

The VPH Method should be used with caution at sites with an uncertain history, particularly closed or abandoned Manufactured Gas Plants (MGPs). Styrene, a common contaminant of concern (COC) at many MGP sites, cannot be satisfactorily resolved from o-xylene under the chromatographic conditions specified for the VPH Method. If encountered, co-eluting styrene could cause an overestimation of o-xylene and a subsequent underestimation of the C₉-C₁₀ aromatic range when the overestimated o-xylene peak is subtracted from the PAC for the range. Other contaminant pairs routinely encountered at MCP sites that are difficult to resolve under the chromatographic conditions specified for the VPH Method include 1,2-dichloroethane/benzene and 1,1,1,2-tetrachloroethane/ethylbenzene.

2.1.3 Evaluation of Interfering Compounds Not Associated with a Petroleum Product

In general, it may be prudent to confirm all PID/FID data by SW-846 Method 8260B (GC/MS) if critical MCP decision making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the VPH Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with VPH in either an aliphatic or aromatic fraction or with a Target Analyte, and such interference would adversely affect MCP decision making, if confirmed, then SW-846 Method 8260B, Volatile Organics by GC/MS (WSC-CAM-II A) should be employed to accurately identify and quantify the components that comprise the fraction or to resolve the analyte pairs.

It is recommended that the chromatographic conditions specified under SW-846 Method 8260B be modified for consistency with the conditions specified by the VPH Method to better allow for a direct comparison of the suspect PID/FID peaks with the GC/MS system. This is particularly useful when comparing suspect aliphatic hydrocarbons. The electron impact mass spectra for aliphatic hydrocarbon homologues are not particularly unique and chromatographic relative retention time data may also be required to confirm VPH data.

2.1.4 PID Response to Non-Aromatic Compounds

Although not a predominant component in petroleum hydrocarbon mixtures, alkenes and other non-aromatic hydrocarbons can elicit a positive PID response. In general, the PID response to these non-aromatic compounds is weaker than the response for the same mass of an aromatic hydrocarbon. However, at elevated concentrations, these non-aromatic compounds may interfere or yield false positives (high positive bias) to aromatic target analytes or range



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concentrations. This condition can be somewhat mitigated by using a lower energy lamp in the PID assembly of the gas chromatograph. Such a change would result in a loss of sensitivity and is considered a major instrument modification that would require re-calibration, a re-demonstration of performance and documentation in the Environmental laboratory case narrative.

2.2 Substitution of GC/MS for the Identification and Quantification of VPH Ranges and Target Analytes

Consistent with Section 11.3.1.1 of the VPH Method, substitution of GC/MS for conventional GC detection for the quantification of VPH ranges is considered a "significant modification". Modifications to the VPH Method are permissible, provided that adequate documentation exists or has been developed, to demonstrate an equivalent or superior level of performance. Be advised, however, that any adaptation to the VPH Method that constitutes a "significant modification" pursuant to Section 11.3.1.1 will preclude obtaining "presumptive certainty" status for any analytical data produced using such modification and must be disclosed and described on the data report form, as detailed in Section 11.3.1 of the VPH Method.

Any major modification to the VPH Method is deemed to satisfy the requirement "to demonstrate an equivalent or superior level of performance" for the determination of the collective concentrations of specified VPH aliphatic and aromatic ranges in water and soil/sediment matrices when:

1. The analytical data produced by the candidate method modification is in a format that is suitable for the evaluation using the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994 and Updated Draft, 2003);
2. The analytical data produced by the candidate method modification for both the VPH aliphatic and aromatic ranges and target analytes must have the requisite accuracy and precision to be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000) consistent with the analytical data quality requirements of 310 CMR 40.0017;
3. The reported concentration for the C₅-C₈ Aliphatic Hydrocarbon range includes the preponderance of the individual C₅ through C₈ aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment;
4. The reported concentration for the C₉-C₁₂ Aliphatic Hydrocarbon range includes the preponderance of the individual C₉ through C₁₂ aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment; and
5. The reported concentration for the C₉-C₁₀ Aromatic Hydrocarbon range includes the preponderance of individual C₉ through C₁₀ aromatic hydrocarbon compounds



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contained in the subject petroleum product in the matrix of interest associated with a release to the environment.

3.0 Reporting Requirements for the VPH Method

3.1 General Reporting Requirements for the VPH Method

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in CAM VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory case narrative contents in WSC-CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for the VPH Method

Specific Quality Control Requirements and Performance Standards for the VPH Method are presented in Table IV A-2. Specific reporting requirements for the VPH Method are summarized below in Table IV A-4 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.



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Table IV A-4 Routine Reporting Requirements for the VPH Method

Parameter	VPH Method Reference	Required Analytical Deliverable
GC Performance	10.2.1	NO
Retention Time Windows	10.2.2	NO
Initial Calibration	10.2.3	NO
Calibration Check Standard	10.4.2.1	NO
Laboratory Method Blank	10.4.2.2	YES
Laboratory Control Sample (LCS)	10.4.2.3	YES
LCS Duplicate	10.4.2.4	YES
Field Matrix Spike (MS)	10.4.3.1	YES (if requested by data user)
Field Matrix Spike Duplicate (MSD)	10.4.3.1	YES (if requested by data user)
Field Matrix Duplicate (MD)	10.2.2.4	YES (if requested by data user)
Surrogates	10.4.1	YES
General Reporting Issues	11.3	Required data reporting content is presented in Section 11.3 of the VPH Method

3.2.1 Correction of VPH Soil and Sediment Data for Percent Moisture

As described in Section 9.1.6.1 of the VPH method, soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

3.2.2 Data Correction for VPH Concentration Calculations for Methanol Preservation Dilution Effect for Soils and Sediments

Based on the requirements of Section 9.6.2.2 of the VPH Method and Section 11.10.05 of SW-846 Method 8000C, VPH analytical results for soil and sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting VPH concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases, if this correction is neglected.

VPH concentrations and the recovery of matrix spikes and/or surrogates in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the



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assumption that 1 g of water occupies a volume of 1 mL). This is a conservative correction regarding calculated VPH concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical-binding forces.

The total solvent/water volume (Vt) is calculated using the following equation:

$$\text{mL solvent/water (Vt)} = \text{mL of methanol} + ((\% \text{ moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value shown in Equation 7 and 8 in Section 9.6.2 of the VPH Method. It should be noted that whether corrected or uncorrected, the Vt value used to calculate VPH concentrations must also take into consideration the volume of any surrogate/spiking solution added to soil/sediment samples.

3.2.3 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the VPH target analytes or ranges exceed the concentration of their respective highest calibration standard, or any non-target peak exceeds the dynamic range of the detector (i.e., "off scale"), the Reporting Limit (RL) for each VPH target analyte or range must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$\text{DF} = \frac{\text{Sample Aliquot Volume (mL)} + \text{Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

$$\text{RL}_d = \text{DF} \times \text{Lowest Calibration Standard for Target Analyte}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enables quantification of target analytes or ranges, which exceed the calibration range. All dilutions must be fully documented in the Environmental Laboratory case narrative.

Analytical Note: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte must be at least 60 to 80% of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes, which did not require dilution.

If a sample analysis results in a saturated detector response for any target or non-target compound, the analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank demonstrates the lack of system interferences.



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Title: Sample Collection, Preservation and Handling procedures for the VPH Method

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for VPH samples analyzed in support of MCP decision-making are summarized below and presented in Section 8.3, Table 4 of the VPH Method. The VPH preservation method selected should be based on the data quality objectives of the sampling program.

Matrix	Container ¹	Preservation	Holding Time
Aqueous Samples (using ambient temperature purge)	2 x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light	Add 3 to 4 drops of 1:1 HCl to pH <2; Cool to 4 ± 2° C	14 days
Aqueous Samples (using heated purge) ²	2 x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light	Add 0.40 to 0.44 grams of trisodium phosphate dodecahydrate to pH >11; cool to 4 ± 2° C	14 days
Soil/Sediment Samples ³	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil/sediment 40-mL vials: add 15 g soil/sediment	1 mL methanol for every g soil/sediment; add before or at time of sampling; cool to 4°C ± 2°C	28 days

1. The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

2. Heated purge is considered a significant modification to the method, as per Section 11.3.1.1.

3. Refer to Appendix 4 of the VPH method for details on sample collection or optional collection/storage devices.

Additional Sampling Considerations

Aqueous Samples

If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. In these instances, the analysis holding time is seven (7) days from date collected to date analyzed.

Solid Samples

Samples may be collected in a hermetically sealed sampling device, such as an EnCore™ sampler. EnCore™ samplers may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A. The laboratory must transfer the contents of the EnCore™ sampler to a pre-weighed vial and preserve the sample in methanol within 48 hours of sample collection. The sample must be analyzed within 14 days of sample collection. The EnCore™ samplers must be kept at 4°C from time of collection to time of preservation. The preserved samples must be kept at 4°C from time of preservation until the time of analysis.

An extra aliquot of sample must be collected in a 4 oz. glass jar with no preservative so that the laboratory can perform a percent solids analysis. If the same sample is being submitted to the laboratory for additional analyses, which require no preservative, the percent solids analysis can be measured using an aliquot from these bottles. Otherwise, a separate bottle will be needed.



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Title: Example Calculation Work Sheet for the VPH Method

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